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SEMI-CONDUCTOR PHOTON DETECTORS: A REVIEW OF THE LITERATURE AND--ETC(U)
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(6) SEMI-CONDUCTOR PHOTON DETECTORS:

A REVIEW OF THE LITERATURE AND

AN EVALUATION FOR SPECTROCHEMICAL APPLICATIONS.

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ABSTRACT

The operational characteristics of current semi-conductor photon detectors are reviewed. Particular attention is paid to comparison of these experimental detectors with the conventional photomultiplier tube. The semi-conductor detectors offer significant advantages for multielement analyses in fields such as atomic absorption and atomic emission spectroscopy. Relevant literature is listed and abstracted.

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SEMI-CONDUCTOR PHOTON DETECTORS: A REVIEW OF THE LITERATURE AND AN EVALUATION FOR SPECTROCHEMICAL APPLICATIONS

INTRODUCTION

The principle of photoconduction has become an invaluable asset in the field of instrumental analytical chemistry. Classical methods for the detection and interpretation of spectral information have been centred upon the photographic plate and the photomultiplier tube, which transforms light intensity directly to an electronic signal. The photomultiplier tube has the obvious advantage over the photographic plate of instantaneous recording, but the selectivity of the photomultiplier tube does not make it well-suited for simultaneous multielement analyses. A recently developed alternative to the photomultiplier tube is the semi-conductor detector. The continuous nature of a semi-conductor photon detector allows for simultaneous measurement at numerous wavelengths, and a virtual electronic replacement of the photographic plate can thereby be achieved. In this report an attempt has been made to outline the various semi-conductor devices presently available and to point out their advantages over the conventional photomultiplier tube, as well as their potentialities in spectrochemical research.

THEORY OF PHOTOCONDUCTION

Radiation falling on a semi-conductor material can produce electron-hole pairs in the material which can be used as charge carriers. There are two limiting wavelengths for the useful radiation, one where the photon energy is not great enough to cause excitation of electrons from the valence band to the conduction band, and one where the photon energy is too great and will cause the electron to be emitted from the surface. By doping the semi-conductor material with another substance, the energy required to promote electrons can be lowered and, by choosing a suitable doping level, a practical device can be constructed to respond to a particular range of wavelengths. If the radiation generates electron-hole pairs near a PN junction, the electric field of the depletion layer at the junction will separate the electrons and holes, thus giving rise to a short-circuit current or an open-circuit voltage. This photovoltaic effect is the fundamental basis of the practical application of photodiodes and phototransistors.

The performance of a photoconductive detector is limited by noise. The noise in the detector itself is produced by the thermally-generated carriers in the semiconductor material. At very low levels of incident radiation, the thermally-generated carriers may swamp the photo-generated carriers. This effect can be minimized by cooling the detector to liquid nitrogen or liquid-helium temperatures if necessary. There is, however, a theoretical limit to the performance of the detector set by the thermal background radiation.

THE DEVELOPMENT OF ELECTRONIC IMAGE SENSORS

A very large number of spectrochemical measurements would be greatly facilitated if effective detection systems were available that combined the desirable characteristics of the photomultiplier tube (wide linear dynamic range and sensitivity and the fact that it transforms light intensity directly to an electronic signal) with the one major advantage of the photographic plate, that of simultaneous multichannel spectral detection. The development of such electronic image sensors has been a source of great activity in the past few years, and has been comprehensively reviewed by Horlick.[33]

The initial electronic image sensor produced, the image orthicon, consists of three distinct elements: a radiation sensor (photo-cathode), a charge storage element (frequently a thin film of MgO), and a readout system (scanning electron beam). The secondary electron conduction (SEC) image tube has a somewhat similar construction except that the charge storage element is a multilayer target of Al_2O_3-Al-KCl and the scanning electron beam readout operates in the so-called direct beam mode, as opposed to the return beam mode of the image orthicon. Further development led to the vidicon detectors. Vidicon is a generic name for electronic image tubes that use a single element which combines the radiation sensor and charge storage functions (Figures 1 and 2). Readout is still accomplished using a scanning electron beam. These vidicon tubes include the Plumbicons and the silicon diode array camera tube or silicon vidicon. The characteristics of these and various other electron beam image tubes are compared in Table I.

The most recent developments in electronic image sensors are devices which combine all the basic functional elements (radiation sensor, charge storage, and readout) into a single integrated circuit. The two main

devices of this type are self-scanning silicon photodiode arrays and charge coupled devices (CCD), both of which are available in linear and area array configurations. The photodiode arrays in particular have superior performance when compared to most other electron image sensors. The characteristics of the various solid-state image devices are compared in Table II.

OPERATIONAL CHARACTERISTICS

Silicon Vidicon Tube

Basically, part of the spectrum exiting from a monochromator is dispersed across a light-sensitive target to produce a charge pattern. This charge is read by a scanning electron beam, and the charge density at each point on the target is obtained (Figure 1). The charge density is a function of radiation intensity, and the position is a function of wavelength. The target (Figure 2) consists of an array of P-type semi-conductor islands grown on an N-type silicon wafer to form a mosaic of photodiodes. The regions between the P-type islands are coated with silicon dioxide to shield the N-type silicon wafer from the electron beam.

During operation the electron beam scans the tube target, charging the P-type islands to the negative potential of the electron gun. Application of a positive voltage to the N-type substrate causes the diodes to be reverse biased. Because of the insulating properties of the depletion layer formed in reverse biased diodes, each diode acts as a storage capacitor. Photons absorbed by the N-type silicon wafer produce electron-hole pairs. The holes produced in this manner diffuse through the depletion layer into the neighbouring P-type islands, discharging the capacitors in those regions exposed to light. This makes these P-islands relatively more positive than those where photon-induced holes have not been collected. No output signal results when the scanning electron beam scans over a region which has not lost its negative charge from the previous scan. An output signal is generated, however, when the scanning beam passes over those regions which have partially lost their initial negative charge either by leakage or photo-induced hole collection. The displacement current produced during the recharging of these partially discharged capacitors is amplified as the signal. By delaying the scanning electron beam, integration on the vidicon target is possible.

Of the image detectors available, the most useful vidicon tubes for the analytical chemist will probably be the silicon tube, the silicon

intensified target (SIT) tube, and the secondary electron conduction (SEC) tube. The SIT is useful for measuring low light levels, since it provides a higher gain than both the standard silicon vidicon and the SEC vidicon. The SEC, however, has a much lower dark (leakage) current, permitting long integration by accumulating charge on the target without seriously affecting the signal-to-noise ratio. The SIT is more expensive than the SEC, but it is also far more robust and less likely to be damaged from overexposure. (See, again, Table I for a comparison of the characteristics of these devices.) For atomic absorbtion spectrometry, the silicon vidicon is probably adequate (Figure 3), and in this application the higher cost of the SIT and SEC vidicons would not be justified. However, for atomic emission and atomic fluorescence, where low light levels must often be detected, a SIT or SEC tube with its higher gain would be preferable.

Many electron beam image tubes, for best conversion of visual information, are designed to have a limited dynamic range, a limited spectral range, and even a non-linear intensity response. As well as this, readout remains somewhat complicated in that an electron beam must be scanned over a two-dimensional surface in order to read out the image information. Although the silicon vidicon has a better dynamic range than previous television sensors, the readout is still accomplished utilizing a scanning electron beam. Most of the above complications with conventional television-type sensors have now been overcome by the development of self-scanning linear silicon photodiode arrays.

Solid-State Photodiode Arrays

Two types of imaging detectors are available:

1) devices requiring a scanning electron beam for interrogation of the active surface, such as vidicon tube; and
2) solid-state imaging devices that do not require an electron beam, such as the self-scanning photodiode arrays. Solid-state image array detectors operate in the same manner as the camera tubes but without the problems introduced by the moving electron beam.

The solid-state image array detector consists of an array of silicon photodiodes packaged in a conventional dual-in-line integrated circuitry. Two basic signals are required to scan the photodiode array -

a start pulse and a continuous series of clock pulses. The start pulse initiates the scan of the photodiode array and is followed by 256 clock pulses (for a 256 element array) which sequentially sample each of the individual photodiodes. Since the photodiodes operate in a charge storage mode, the signal level on a diode when it is read out by a clock pulse during a scan represents the time integral of the light intensity falling on that specific diode since a clock pulse was applied to it during the previous scan. To utilize the integrating characteristic of the charge storage mode of operation, successive start pulses can be delayed for perhaps several thousand clock pulses.

Both the control and measurement electronics (excluding the computer) are simple, inexpensive, and readily available. The arrays themselves are very compact and rugged and are easily mounted in essentially any desired system, and require little power for their operation. Their most attractive features include: solid-state (silicon) reliability, that is, very stable geometric, radiometric, and electrical characteristics; excellent response of silicon in the vacuum UV to near IR range; digital scanning which provides geometric accuracy; high versatility in addressing and in some cases random access capability; compactness and flatness which provide unusual interfacing flexibility and simplified cooling; and a predicted substantial reduction in future cost.

The arrays show essentially no tendency to bloom. Blooming, in electronic image sensors, refers to the situation where a strong signal spreads to adjacent sensor elements. In spectrometric applications, even minor blooming of the electronic image sensor can seriously degrade resolution and/or severely limit the use of the integrating capability of the sensor in measuring weak spectral lines in the presence of strong lines. Both silicon vidicons and the charge coupled devices have problems with blooming. With photodiode arrays, the integration time can be used to increase the sensitivity for weak lines and intense lines will not interfere because of blooming even if they strongly saturate the array. Figure 4 illustrates this point very clearly. The weak lines of the spectrum (of a Ne-filled hollow cathode lamp) are clearly resolved after the long integration period, even though they are close to very intense lines.

Another important characteristic of electronic image sensors is lag. Lag refers to image carry-over from one frame (integration time) to the

next. With the silicon vidicon, for example, only 90% of the image may be erased on a readout cycle. Lag is undesirable and can be particularly bothersome if the sensor is being used for time-resolution studies. Photodiode arrays, on the other hand, do not appear to exhibit any lag.

The self-scanning silicon photodiode array comes very close to providing the characteristics necessary for an all-electronic replacement of the photographic plate.

COMPARISON TO PHOTOMULTIPLIER TUBES

The major advantage of these electronic image detectors over conventional photomultipliers is their applicability to multielement analysis. The continuous nature of the vidicon tube and photodiode array allows numerous spectral lines to be simultaneously monitored. This provides the opportunity for multiple-analyte, internal standard methods in flame spectrometry. (Figure 5 displays a multielement flame emission spectrum.) Because of the rapid data acquisition scheme, analyses require much less operation time. They are then subjected to fewer instrumental fluctuations thus improving the accuracy and precision of measurement.

The data obtained from these detectors are readily amenable to computerization. Signal averaging techniques improve precision and allow the removal of practically all types of spectral interferences. Figure 6 demonstrates computerized noise removal, and Figures 7 and 8 show how overwhelming spectral interferences can be "stripped" away to uncover the desired signal. The intimate electronic control of the detector allows for quick changes of the spectral lines being monitored, and it is simple to change the elements being determined. The ability to vary the integration time for different lines permits the analysis of samples for elements present in widely different amounts without dilution. The simultaneous determination of a large range of wavelengths and the electronic control capabilities of these detectors make them a powerful tool. Smoothing, resolution enhancement, and differentiation of spectra can be performed within a matter of minutes, right at the spectrometer.

A number of comparisons between photomultiplier tubes and various photodiodes and phototransistors indicate that, except for wavelength regions in the near infrared at which the photomultiplier sensitivity drops below that of a photodiode, photomultiplier tubes still offer superior performance in the

UV, visible, and near IR wavelength regions in normal applications. The comparative lack of sensitivity of the semi-conductor devices is their major disadvantage. The increased gain of the SIT tube allows for greater sensitivity than the standard silicon vidicon, but they still do not compete with photomultipliers. Detection limits and dynamic ranges (range of saturation current to dark current) are also somewhat poorer, and at high integration times the array can become saturated with dark current. Some atomic absorption (AA) results obtained with a vidicon detector are compared with conventional AA results in Table III.

The primary limitations of these electronic image sensors are limited sensitivity and the compromise necessary between wavelength coverage and reasonable spectral resolution when coupled to conventional dispersive systems. According to Horlick,[33] "It does not appear that effective and inexpensive solutions to these problems are close at hand."

FEASIBILITY AND FUTURE

The multichannel nature of these electronic image detectors makes them particularly well-suited to multielement flame emission or atomic absorption spectrometry. It is necessary only that the analytical lines of the desired elements be within the spectral region covered by the detector. Their use is not confined to line spectra, but spectrometric measurements over the UV - VIS and near - IR regions can be carried out (Figure 9). The photodiode array detector in particular should also be quite useful for time-resolved spectrometry as it can be repetitively scanned at relatively rapid rates (in the μsec. to msec. region).

To undertake high-resolution gamma-ray spectroscopy with semiconductors usually requires very small detector currents. With silicon, these are obtained by operating the detectors at cryogenic temperatures. Another approach is to use materials with larger bandgap energies such as GaAs, CdTe and HgI_2. (Some of the characteristics of these substances are compared in Table IV.) GaAs and HgI_2 have sufficiently low currents at normal operating voltages for low noise operation at room temperature. However, owing to the lack of development in these materials, the silicon and germanium detectors presently remain more accurate and reliable.

High initial cost is a principal factor presently limiting the use of vidicon and solid-state detectors, but solid-state detectors that now

cost approximately $4000 are expected to be reduced to about $50 in 1980, and should then become more widely used.

Table I Characteristics of Electron Beam Image Tubes.

	Sb_2S_3-vidicon	Plumbicon (PbO)	Si-vidicon	ASOS-RBV*	Si-RBV
Format: diam, mm	16, 25	25, 46	16, 25	8, 16, 25	25, 50
Sensitivity, photons/cm²[a]	2.8×10^{10}	4×10^{9}	8.3×10^{9}	8.3×10^{10}	8.3×10^{9}
Max signal to rms, SNR (sat.)	200	320	480	30	
Dynamic range[c]	250 Nonlinear	100 Linear	500–1000 Linear	80 Nonlinear	100 Linear
Resolution: lp/mm MTF = 20%	45	14	32	75	60
MTF = 50%	24	9	18	45	40
No. of resolving picture elements,[e] pixels	4×10^{5}	4×10^{4}	2×10^{5}	13×10^{4}	10^{5}
Spectral response, nm[f]	300–800	380–800[h] 380–600	350–1100	450–850	350–1100
% QE at 300 nm					
400 nm	13	62	68	30[g]	50[g]
600 nm	24	15	78	80	60
800 nm	17	0	82	5	45
1000 nm	15	0	15	0	2
Image retention (lag), %[i]	30	9	14	>50	Not available
Max integration time, sec	0.9	10	>1.0	>1.0	>1.0
Price estimate for standard tube, thousands of dollars	0.1	0.5–1.0	0.3–0.5	Commercially unavailable[k]	Commercially unavailable[k]
Manufacturer	RCA GE Hammamatsu	RCA Phillips Labs	RCA GE Westinghouse Hammamatsu	RCA	RCA

SIT (EBS)**	SEC***		Image orthicon	Image isocon	Electrostatic camera	Image dissector
	Electrostatic	Magnetic				
16, 25, 40	25, 50		40	40	50	19, 43
5.5×10^{7}	8.3×10^{7}		2.5×10^{8}	5.8×10^{7}	1.0×10^{9}	7.2×10^{14}, high resolution 6.0×10^{10}, low resolution
32	90		45	100		1.22 d $\sqrt{E\Delta t}$[b]
500–1000 Linear	~500 Only partial linearity		100 Linear	1000 Linear	1000[d] Linear	10,000 Linear
15	14	30	12	14	50	55
10	8	20	6	10	30	35
6×10^{4}	$2\text{–}4 \times 10^{4}$		6×10^{4}	2.0×10^{5}	6×10^{5}	$2\text{–}4 \times 10^{5}$
360–850	300–800	100–900	300–800	300–775	300–800	350–850
			4[g]	18[g]	60[g]	
15	12		100	100	60	15
9	5		16	54	40	5
0.3	0.8		0	1.8	1.0	0.3
0	0		0	0	0	0
15	6		10	10[f]	[j]	20
>1.0	>5 hr		>1.0	>1.0	Hundreds of hr	0
1.2–1.5	1–2	3–5	1–2	2–3	>10	1–5
RCA GE	Westinghouse		RCA GE	RCA GE	CBS Labs	ITT Westinghouse EMR

[a] Sensitivity is defined for SNR = 1 at 550-nm illumination for 1/30-sec integration time. [b] d is the aperture; E, the faceplate illumination in footcandle; and Δt, the dwell time in seconds. [c] Dynamic range refers to the working range and is defined by the transfer characteristics of the tube. [d] Based on a private communication with CBS Laboratories. [e] Number of pixels was determined assuming a square format of the target and resolution at 50% MTF. [f] The spectral range given for the standard tubes. Different ranges can be achieved with these tubes if different window materials and photocathodes are used. [g] These figures are based on relative response rather than % QE. [h] This extended spectral range is obtained with PbO-PbS rather than PbO target. [i] Lag is defined as signal remaining on target after one readout of a 200-nA signal at standard TV rates. [j] Lag is insignificant here since functions of exposure, storage readout, and erasures are totally separated. [k] These tubes were specifically designed for NASA. [l] Lag is defined as signal remaining on target after third readout.

*Antimony Trisulfide Oxysulfide-Return Beam Vidicon
**Silicon Intensified Target
***Secondary Electron Conduction

Table II Characteristics of Solid-State Image Devices.

	Silicon photodiode arrays	Charge coupled devices (CCD)	Silicon photodiodes with CCD readout	Charge injection devices (CID)
Format, no. of pixels (elements)	Linear arrays: 128–1872[f] elements. Area arrays: 32 × 32 and 50 × 50	Linear arrays: 256–1728. Area arrays: 100 × 100 and 320 × 512	Linear arrays: 128, 256, and 512	Area arrays: 100 × 100 and 188 × 244
Pixel size, μm	25.4 × 25.4 to 25.4 × 432. 25.4 center-to-center (ctc). 15 ctc for 1872 array	13 × 17, 30.5 × 30.5 (Fairchild), 25–125 length (RCA). 30 ctc	18 ctc × 10 width	31.5 × 61[f]
Sensitivity,[b] photons/cm²	1.8×10^7 to 3×10^8	Linear: 1.3×10^8 to 4×10^8. 100 × 100: 7×10^7	2.2×10^8	10^8
Saturation exposure, photons/cm²	2.4×10^{10} to 5×10^{11}	Linear: 4×10^{10} to 6×10^{10}. Area: 1.3×10^{10}	4×10^{11}	5×10^{11}
Dynamic range	1000–20,000[g]	200–400	200–500	500
Noise,[c] electrons/pixel	1000–2000	1000	1.0 mV[k]	5000[m]
Dark noise,[d] electron/pixel	>1000	5–10 mV[k], ~300–1000	1.0 mV[k] (dark noise not available)	3000–4000
Integration time, (sat. time by dark current), sec	At 25°C: 1. At −40°C: 500	At 25°C: 1–2. At −40°C: 30–90	At 25°C: 0.5–1	At 25°C: 1–2. At 40°C: 240
Clock rate, MHz	Min consists with integration time. Max: 10	0.05–10	0.01–2	0.05–4
Resolution,[e] % MTF	58	40–60	66	85
Manufacturer	Reticon	Fairchild, RCA, Bell Northern Research[h]	Bell Northern Research	General Electric
Availability	Off the shelf	Now	Now	Now
Cost	$750 for 256 × 1 array. Other sizes, price is proportional to number of pixels. 1872 pixels ~ 3800	Linear: $275–1500. Area: 100 × 100: $965 (Fairchild), 320 × 512: $3800 (RCA)[j]	Price available from company upon request	$6500[j]

[a] The reader is advised to use the data given in this table very cautiously because: the data are based on information gathered only from the manufacturers; it is not easy to compare these devices because the characteristics demanded by a particular application are important; and the various manufacturers disagree on the definition of a few parameters (in particular, sensitivity, noise, and dark noise). [b] Sensitivity is defined as the exposure (at 550 nm) level at which the signal level equals the peak-to-peak random noise level. [c] Noise is measured within the video period of each pixel period and at a specified (by manufacturer) test frequency. Main noise source is input capacitance noise. [d] This value refers to the shot dark noise rather than to the dark current. [e] Resolution is given as % MTF at the Nyquist limit spatial resolution (see definition of aliasing) and for visible light. It will be worse for IR illumination. [f] Soon to be announced. [g] Dynamic range will depend on amplifier used. This capability is supposedly achieved because of the larger storage capability available. [k] This value refers to the average dark current rather than to dark noise. [h] This company offers a 100 × 100 pixel area CCD. [j] Price includes camera. [k] Value expressed in electrons/pixel was not available. [f] This and all other parameters below are given for the 188 × 244 CID imager. [m] A new amplifier, now being designed, is expected to lower this value by a factor of three.

Table III Comparative Results by Single-Element AA. Vidicon vs Techtron AA-120

Element and wavelength, nm	Concn at which RSD determined, ppm	Vidicon			Techtron AA-120		
		Sensitivity,[a] ppm	RSD, %	Detection[b] limit, ppm	Sensitivity,[a] ppm	RSD, %	Detection[b] limit, ppm
Zn 213.9	0.5	0.03	3.5	0.01	0.03	0.42	0.005
Pb 217.0	10.0	0.5	1.1	0.4	0.5	0.49	0.2
Cd 228.8	1.0	0.05	2.6	0.04	0.04	0.46	0.005
Ni 232.0	10.0	0.4	1.9	0.3	0.2	0.25	0.05
Co 240.7	10.0	0.4	2.7	0.3	0.4	0.78	0.03
Fe 248.3	5.0	0.3	5.2	0.3	0.3	1.1	0.07
Mn 279.5	2.0	0.1	1.8	0.09	0.1	0.63	0.01
Pb 283.3	10.0	0.9	5.0	0.5	0.9	0.48	0.1
Mg 285.2	0.5	0.02	2.0	0.01	0.01	0.39	0.001
Cu 324.8	2.0	0.1	1.8	0.07	0.1	0.51	0.01
Ag 328.1	5.0	0.1	2.1	0.1	0.1	0.53	0.009
Ag 338.3	5.0	0.2	2.6	0.2	0.2	0.48	0.02
Cr 357.9	10.0	0.4	4.3	0.1	0.2	0.37	0.02
Ca 422.7	5.0	0.2	1.7	0.08	0.1	0.65	0.006

[a] 1% absorption. [b] S/N = 2/1.
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Table IV Comparison of Semiconductor Detectors.

Material	Band gap, eV	Temp, K	Energy per e-h pair, eV	Reverse current or conductivity
Si	1.12	300	3.61	$I_R = 10^{-6}$ A
	1.16	77	3.76	$I_R = 10^{-13}$ A
Ge	0.74	77	2.98	$I_R = 10^{-11}$ A
GaAs	1.4	295	4.2	$I_R = 5 \times 10^{-9}$ A
CdTe	1.47	300	4.43	10^{9} ohm-cm
HgI_2	2.13	300	6.5	10^{13} ohm-cm

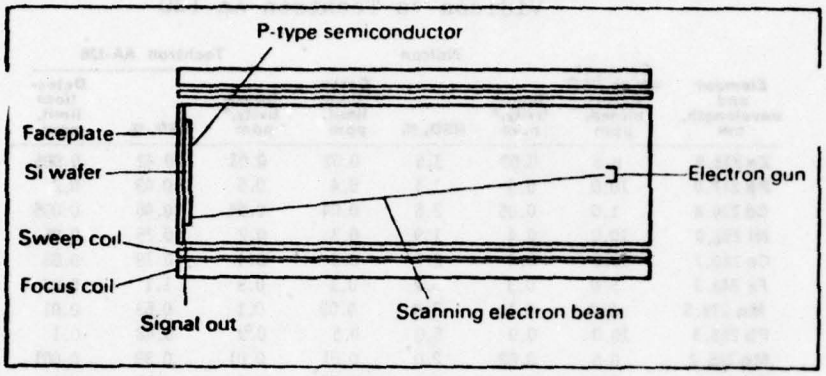

Figure 1. Silicon Diode Vidicon Tube Detector for Multielement Analysis.

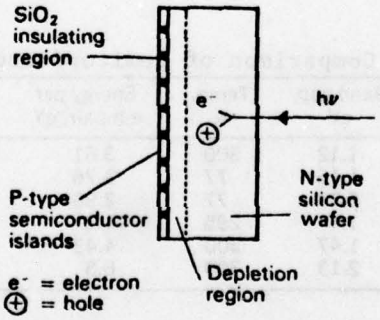

Figure 2. Target for Silicon Vidicon Tube.

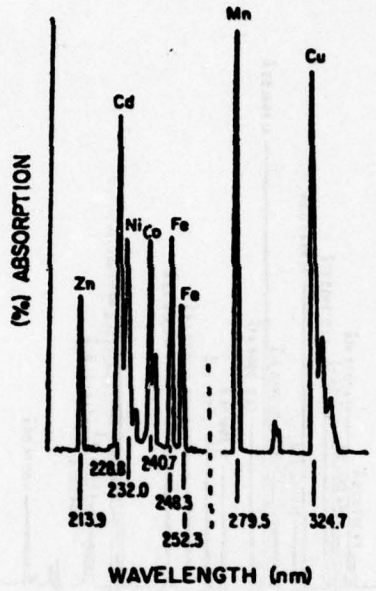

Figure 3. Vidicon AA Spectra for Seven Metals Extracted from a Multielement Aqueous Standard (0.2 µg/ml) into MIBK.

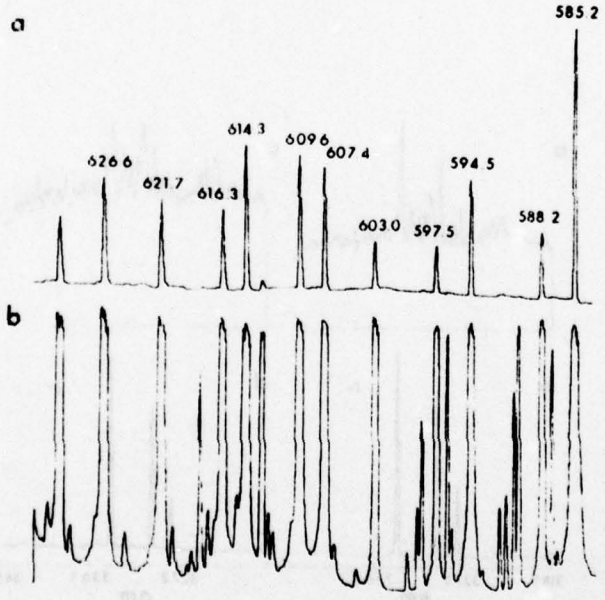

Figure 4. A Comparison of the Integration Performance of a Cooled Array.
a) 0.18 sec.
b) 23.3 sec.

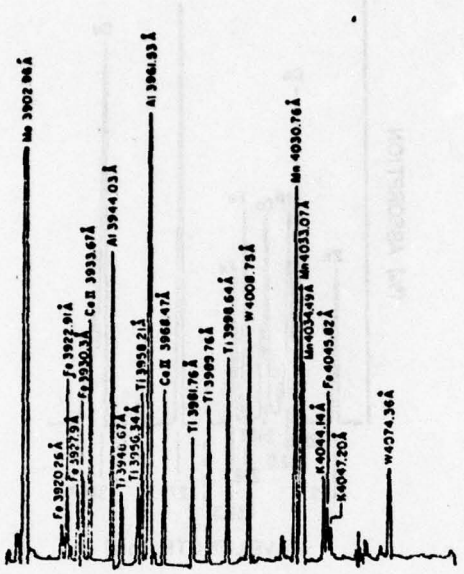

Figure 5. Multielement Flame Emission Spectrum from 3886 to 4086Å.

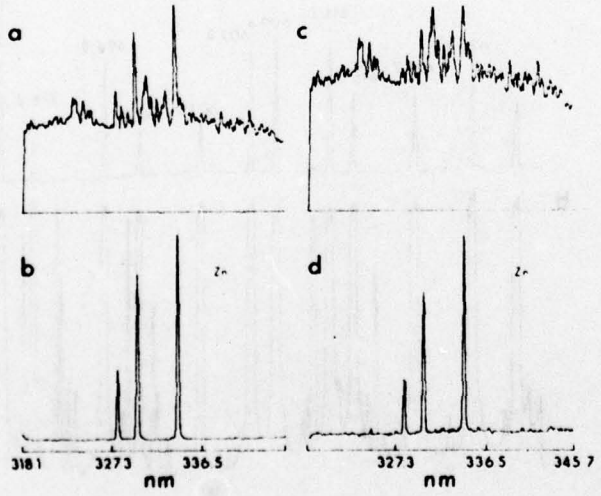

Figure 6. Spectra Illustrating the Power of Electronic Background Subtraction.

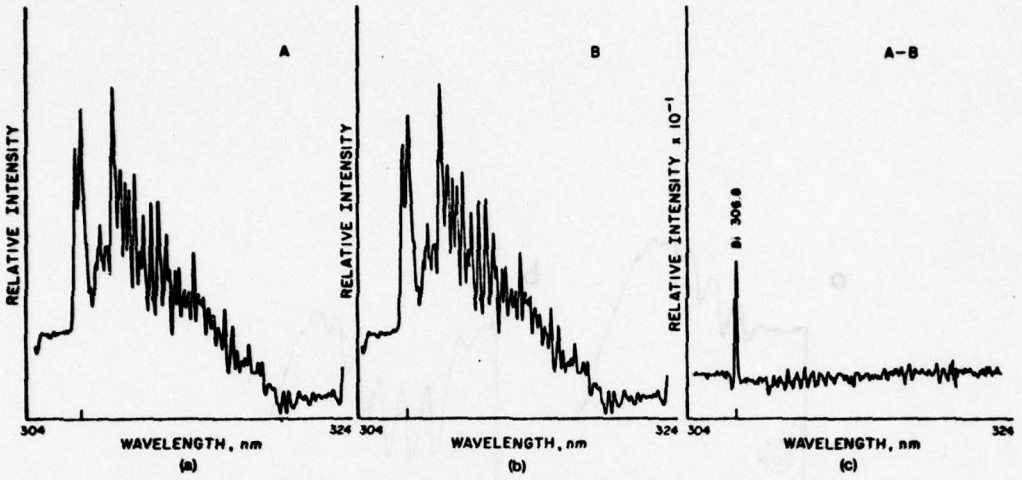

Figure 7. Interference of OH Flame Bands with Bi 306.8 nm Line
a) Spectrum obtained with 60 ppm Bi solution in N_2O-C_2H_2 flame, and stored in memory A.
b) Spectrum of OH flame bands under identical experimental conditions and stored in memory B.
c) Net spectrum of Bi obtained using A-B mode, where intensity scale divided by 10 to clarify signal.

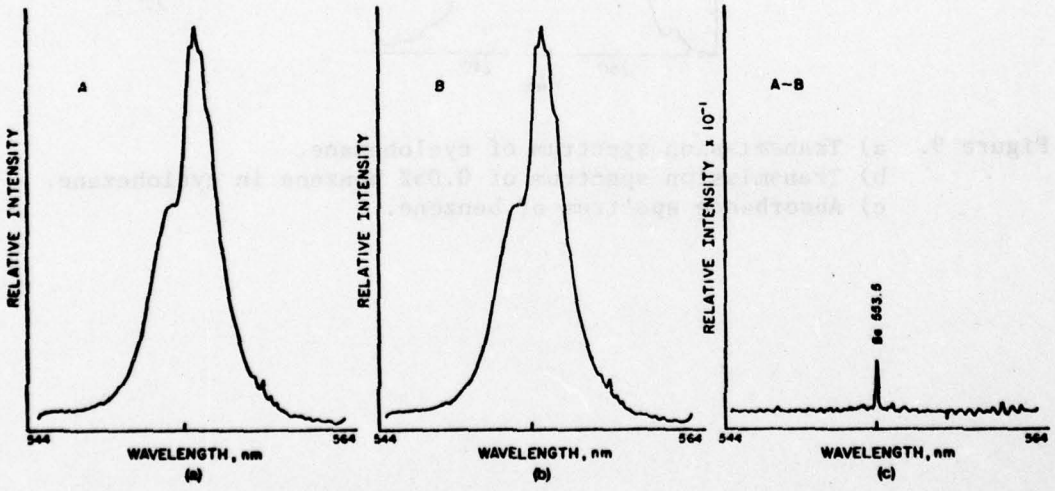

Figure 8. Interference of CaOH Band with Ba 553.5 nm Line.
a) Spectrum from solution containing 0.35 ppm Ba and 165 ppm Ca - stored in memory A.
b) Spectrum in memory B after spectral stripping using a Ca stripping solution.
c) Net spectrum of Ba obtained using A-B mode - intensity scale divided by 10 to clarify signal.

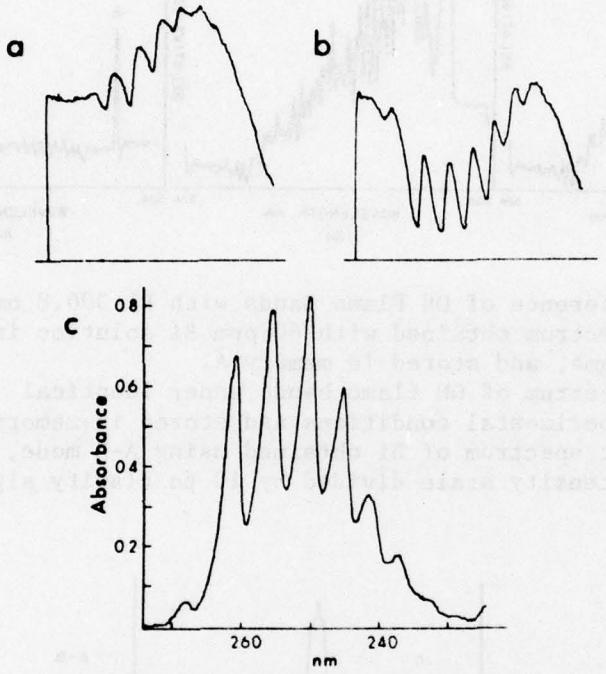

Figure 9. a) Transmission spectrum of cyclohexane.
b) Transmission spectrum of 0.05% benzene in cyclohexane.
c) Absorbance spectrum of benzene.

BIBLIOGRAPHY & ABSTRACTS

1. Ingle J.D. and Crouch S.R., "Signal-to-Noise Ratio Comparison of Photomultipliers and Phototubes", Anal. Chem. 43, 1331 (1971).

This study uses signal-to-noise ratio (S/N) characteristics to decide when it is best to use either a photomultiplier or photodiodes. Many factors must be considered in choosing the optimum transducer-amplifier system for a given spectrometric application. Dynamic range, linearity, and response speed must all be considered in addition to the inherent signal-to-noise characteristics. In this paper, however, only the S/N characteristics of photomultipliers and photodiodes are compared. Equations are given for determining S/N from the parameters involved, thereby indicating which system is best for a given application.

2. Santini R.E., Milano M.J., Pardue H.L., and Margerum S.W., "A Swept Electron Beam Rapid Scan Spectrophotometer - Some Qualitative Aspects", Anal. Chem. 44, 826 (1972).

This is an early report on the use, and possible future applications, of a vidicon television camera pick-up tube. Some theory on the construction and operation of the tube is also presented. In using the tube, they are utilizing "... techniques which were originally intended for video applications".

3. Barnes R.M. "Emission Spectrometry", Anal. Chem. 44, 122R (1972).

This is a review article on Emission Spectrometry. It contains comparisons of photomultipliers and photodiode detection systems and many related references. The echelle grating is mentioned, which permits the display of wide spectral ranges in a compact view area.

4. Santini R.E., "Some Comments on the Signal-to-Noise Characteristics of Real Photomultiplier and Photodiode Detection Systems", Anal. Chem. 44, 1708 (1972).

The author disagrees with what Ingle and Crouch say in Reference #1. Santini claims that photomultiplier tube noise characteristics must depend on additional variables which weren't considered. He goes on to say that the low gain amplifier combination is probably not as favorable as it appears in their treatment, and for data collections over prolonged intervals of one hour or more, the photomultiplier exhibits unavoidable, uncontrollable drifts. He favors photodiodes.

5. Ingle J.D. and Crouch S.R., "Signal-to-Noise Ratio Comparison of Photomultipliers and Phototubes", Anal. Chem. 44, 1709 (1972).

Ingle and Crouch defend their earlier work Reference #1, from Santini's attacks in Reference #4. They state that the photomultiplier generally has a significant signal-to-noise ratio advantage.

6. Busch K.W., and Morrison G.H., "Multielement Flame Spectroscopy", Anal. Chem. 45, 712A (1973).

The various approaches currently under study to achieve multielement capability in flame spectrometry are reviewed. The advantages and disadvantages of numerous detection systems are listed, including vidicon detectors. There is extensive theory presented on the operation of the silicon diode vidicon tube detector.

7. Santini R.E., Milano M.J., and Pardue H.L., "Rapid Scanning Spectroscopy: Prelude to a New Era in Analytical Spectroscopy", Anal. Chem. 45, 915A (1973).

Recent advances in opto-electronic systems, including the vidicon tube and solid state detector are discussed. Factors such as size, cost, ruggedness, and service lifetime will favor the solid state devices. Major limitations of the currently available array detectors are also presented, including their low sensitivity in the visible and ultra-violet regions.

8. Mitchell D.G. Jackson K.W., and Aldous K.M. "Application of a Silicon-Target Vidicon Detector to Simultaneous Multielement Flame Spectrometry", Anal. Chem. 45, 1215A (1973).

Atomic absorption spectrometry is the main subject of interest. A vidicon detector enables the rapid simultaneous determination of 10 or more elements in solution. The useful characteristics of the silicon vidicon, silicon intensified target vidicon (SIT), and secondary electron conduction (SEC) vidicon tubes are compared and evaluated. According to the author, the silicon vidicon is probably adequate for atomic absorption, and the higher cost of the SIT and SEC vidicons would not be justified. However, for atomic emission and atomic fluorescence, where low light levels must often be detected, an SIT or SEC tube with its higher gain would be preferable.

9. Horlick G. and Codding E.G., "Some Characteristics and Applications of Self-Scanning Linear Silicon Photodiode Arrays as Detectors of Spectral Information", Anal. Chem. 45, 1490 (1973).

The basic mechanical, optical, and electronic characteristics and features of photodiode arrays as spectrometric detectors are presented. Basic clocking circuits are discussed as well as readout systems. The advantages of photodiode arrays over previous detectors are listed and it is concluded that the photodiode array has many of the desired characteristics necessary for an all-electronic replacement of the photographic plate.

10. Horlick G. and Codding E.G., "Analog Cross Correlation Readout System for a Spectrometer Using a Silicon Photodiode Detector", Anal. Chem. 45, 1749 (1973).

Smoothing, resolution enhancement, and differentiation of spectra can be carried out using cross correlation techniques. The application of a self-scanning linear silicon photodiode array detector to a spectrometer has facilitated the development of a real time analog cross correlation readout system. By utilizing the system presented here, all of the above operations can be performed on spectra right at the spectrometer by cross correlation with an electronic waveform that replaces the conventional mechanical exit slit.

11. Horlick G. Codding E.G., "Dye Laser Intra-cavity Enhanced Absorption Measured Using a Photo-Diode Array Direct Reading Spectrometer", Anal. Chem. 46, 133 (1974).

Enhancement of absorption when a relatively weak and narrow band absorber is placed inside the cavity of a dye laser has recently been reported by several people. The observation of the effect for atomic species in a flame cell inside the dye laser cavity should be particularly important with respect to atomic absorption techniques. Analytical curves are presented for praseodymium and europium.

A key factor in this investigation which greatly facilitated the acquisition of the necessary spectral data was the utilization of a photodiode array direct reading spectrometer. With this instrument, the entire spectrum of a dye laser pulse (~125Å) could be measured and displayed on an oscilloscope essentially instantaneously after firing the dye laser.

Å

12. Milano M.J., Pardue H.L., Cook T.E., Santini R.D. Margerum, D.W. and Raycheka, J.M.T., "Design and Evaluation of a Vidicon Scanning Spectrometer for Molecular Absorption and Atomic Emission Spectrometry", Anal. Chem. 46, 374 (1974).

A silicon target vidicon tube is used for scanning spectrometry in the visible region at speeds ranging from less than 0.1 Hz up to 250 Hz. Quantitative data are reported for kinetic studies using molecular absorption spectrometry and simultaneous multielement analyses in synthetic solutions using flame emission spectrometry.

They disagree with Horlick and Codding in their (H. & C.) dissatisfaction with the vidicon tube. The performance of the silicon target vidicon is shown to be at least as good as the photodiode arrays used by Horlick and Codding in Reference 9. The authors state that adequate information is not available to permit an objective comparison of the two devices. This study demonstrates that the silicon target vidicon is a highly reliable detector for qualitative and quantitative applications in the visible region. It is apparent that a silicon vidicon of some kind will be useful for atomic absorption spectrometry.

13. Busch K.W., Howell N.G. and Morrison G.H., "Vidicon Tube as a Detector for Multielement Flame Spectrometric Analysis", Anal. Chem. 46, 575 (1974).

An instrument for multielement flame emission analysis is described which consists of a 0.5 m Ebert monochromator, a silicon diode vidicon tube, and an optical multichannel analyzer. Optical and electronic considerations of the system are discussed. Using this system, a spectral "window" of 20 nm is monitored simultaneously and atomic lines 1.4 Å apart are resolvable. Detection limits, obtained under compromise flame conditions, are presented for Mo, Fe, Ca, Al, W, Mn, and K using spectral lines present in a single window. The multielement analysis of a geological standard rock sample for Fe, Ca, Al, and Ti is described, and the results are compared with the accepted values.

The authors give the following evaluation of the instrument. "The vidicon detector provides a unique means of simultaneous multichannel detection. Its use, however, is not confined only to flame emission, but should prove useful for multielement atomic absorption and fluorescence as well. In addition to multielement quantitative analysis, the vidicon system should also prove useful in rapid qualitative survey analysis to determine what elements are present in a sample. In single element analysis, the vidicon permits the simultaneous measurement of an internal standard line..." "The vidicon should also prove useful in investigating matrix effects on several elements in a sample simultaneously as well as to monitor changes in background continuum radiation."

14. Lytte F.E., "Measuring Fast Optical Signals", Anal. Chem. 46, 545A (1974).

This study discusses the detection aspect of time-resolved spectroscopic measurements. There is an extensive description of photomultipliers, with comparisons to vacuum phototubes and semiconductor photodiodes.

15. Busch K.W., Howell N.G., and Morrison G.N., "Simultaneous Determination of Electrolytes in Serum Using a Vidicon Flame Spectrometer", Anal. Chem. 46, 1231 (1974).

The rapid simultaneous determination of sodium, potassium, and calcium in blood serum is described using a vidicon flame spectrometer. The system, which includes a silicon-intensified target (SIT) vidicon tube, monitors a 40 nm spectral window. Results for control serum and clinical samples indicate an accuracy and precision of better than 2%. By use of the SIT tube, the weak second-order potassium lines could easily be detected at the concentrations used in this study.

16. Busch K.W., Howell N.G., and Morrison G.H., "Elimination of Interferences in Flame Spectrometry Using Spectral Stripping", Anal. Chem. 46, 2074 (1974).

A simple and rapid spectral stripping technique is described for the elimination of practically all spectral interferences in flame emission spectrometry. The technique utilizes a vidicon flame spectrometer, which permits the simultaneous monitoring of a 20 nm spectral range. Examples are described for the removal of either molecular band or undesired concomitant interferences from analytical lines of interest, with resultant high accuracy of determination. In contrast to compensation methods, spectral stripping allows samples of diverse matrices to be determined using a simple calibration curve obtained with synthesized standards containing only the buffered analyte. The time required to perform spectral stripping is less than one minute per sample. There are some very effective examples shown where the desired spectral line is obtained by stripping away the completely overwhelming background signals.

17. Milano M.J. and Pardue H.L., "Evaluation of a Vidicon Scanning Spectrometer for UV Molecular Absorption Spectrometry", Anal. Chem. 47, 25 (1975).

A silicon target vidicon tube with a fused silica faceplate is evaluated for molecular absorption spectrometry in the visible and near ultraviolet region of the spectrum. The spectrometer is evaluated for the quantitative determination of phenolic compounds based upon difference spectra and is

17. cont'd. applied to the kinetic study of a four-step reaction which involves three different intermediates with lifetimes between ten milliseconds and several minutes. Results obtained in this study demonstrate that the silicon target vidicon is a useful detector for molecular absorption spectrometry in the region between 200 and 800 nm, and that it is a powerful tool for recording time-dependent spectra.

18. Talmi Y., "Applicability of TV-Type Multichannel Detectors to Spectroscopy", Anal. Chem. 47, 658A (1975).

This study compares the performance of existing available multichannel detectors, including: image dissector, image orthicon; image isocon, silicon vidicon and silicon-intensified target tubes, secondary electron conduction tube, silicon photodiode arrays, charge coupled devices, charge injection devices, and intensified solid state imaging devices. This reference, along with Reference 19, provides a good, brief comparison of these detectors.

19. Talmi Y., "TV-Type Multichannel Detectors", Anal. Chem. 47, 697A (1975).

This report describes the principles of operation of the devices discussed Reference 18. Included is a glossary of related terms and two tables summarizing the characteristics of electron beam image tubes and solid state image devices.

20. Aldous K.M., Mitchell D.G., and Jackson K.W., "Simultaneous Determination of Seven Trace Metals in Potable Water Using a Vidicon A.A. Spectrometer", Anal. Chem. 47, 1034 (1975).

A multichannel atomic absorption spectrometer is used for the determination of Zn, Cd, Ni, Co, Fe, Mn, and Cu in potable waters. The resonance lines of these elements are measured simultaneously by dispersing a 168 nm region of the lamp and flame spectrum across a vidicon array detector. Detection limits from 0.004 to 0.02 μg/ml were obtained, with dynamic ranges up to 100 and relative standard deviations of 3% at optimum concentrations. This performance, though poorer than by conventional single channel atomic absorption spectrometry, is adequate for routine monitoring of public water supplies and most waste waters.

21. Fricke F.L., Rose O., and Caruso J.A., "Simultaneous Multielement Determination of Trace Metals by Microwave-Induced Plasma Coupled to Vidicon Detector: Carbon Cup Sample Introduction", Anal. Chem. 47, 2018 (1975).

A preliminary study of the potential applicability of the microwave-induced plasma coupled to a vidicon detector. The multielement emission spectrum is quickly obtained and gives good results.

22. Woodruff W.H. and Atkinson G.H., "Vidicon Detection of Resonance Raman Spectra: Cytochrome C", Anal. Chem. 48,186 (1976).

The objective is to apply vidicon detection techniques to time-resolved resonance Raman experiments. Image intensification is required to attain acceptable vidicon sensitivity. Vidicon dark current is the overwhelming source of noise, but can be virtually eliminated either by cooling the detector or by using short-pulse laser excitation. Spectra obtained using the vidicon are much noisier than conventional spectra, but all of the features observed using photomultiplier detection are also seen in the vidicon-detected spectrum, and the spatial and relative intensity relationships of these features are preserved. The data accumulated suggest that time-resolved resonance Raman experiments are feasible in the nanosecond time range.

23. Howell N.G., Ganjei J.D., and Morrison G.H., "Internal-Standardization in Flame Analyses Using a Vidicon Spectrometer", Anal. Chem. 48, 319 (1976).

Routine application of internal standard measurements to flame analyses is facilitated by the use of a vidicon spectrometer. A matrix interference of about 10% is reduced to a 1% deviation through the incorporation of an internal standard in the determination. While the vidicon tube has previously been used as a detector for multielement determinations, it also provides a rapid, accurate, and efficient means of performing internal standard analyses.

The experimental results show how the ratio technique adequately compensates for matrix effects, thus improving the accuracy and precision of flame measurements. Trace elements can then be determined with minimal sample alteration or matrix duplication.

24. Cook T.E., Pardue H.I., and Santini R.E., "Derivative Spectrometry with a Vidicon Detector", Anal. Chem. 48, 451 (1976).

Past systems in atomic and molecular spectrometry have used mechanical wavelength modulation to generate derivative spectra. In this report electronic wavelength modulation is introduced in conjunction with a vidicon detector system. Although there is a significant background signal in the normal spectrum due to the leakage current in the vidicon, it is relatively flat and contributes little to the first derivative.

25. Ganjei J.D., Howell N.G., Roth J.R., and Morrison G.H., "Multielement Atomic Spectrometry with a Computerized Vidicon Detector", Anal. Chem. 48, 505 (1976).

This study describes the development of an on-line computer system interfaced with a vidicon spectrometer for the rapid and efficient handling of data. Operator input has been minimized while the programming has incorporated such features as automatic least-squares polynomial curve fitting, "spectral stripping", background corrected peak signal measurements, and internal standard corrections.

26. Yates Dennis A., and Kuwana T., "Evaluation of a Self-contained Linear Diode Array Detector for Rapid Scanning Spectrophotometry", Anal. Chem. 48, 510 (1976).

The operational characteristics of the 1024-element linear diode array detector from Reticon Corporation were evaluated and discussed. Attractive features for use in a rapid scanning spectrometer included its fast interrogation times, spectral sensitivity from near UV to near IR, and the fact that it has associated electronics for a self-contained unit. The authors feel that a linear diode array unit has rather limited applications due to its lack of sensitivity, but they predict widespread usage of solid state array detectors because of the attractiveness of being able to electronically (vs mechanically) control all aspects of the spectral acquisition.

27. Nieman T.A., and Enke C.G., "Development and Characterization of a Computer-Controlled Vidicon Spectrometer", Anal. Chem. 48, 619 (1976).

A computer controlled spectrometer using a silicon vidicon multichannel detector has been developed to examine the operating characteristics of imaging devices as spectrometric detectors.

Under computer control, the number of electronic channels in the wavelength window can be set between 32 and 4096. The readout beam can be deflected to any channel at random, made to

27.cont'd. scan them sequentially, or inhibited to increase the target's integration time and enhance weak signals. The system has a single scan signal-to-noise ratio (S/N) of 220 which has been extended to 10^4 with signal averaging. S/N increases linearly with target integration time up to at least a 20-fold enhancement. The detector responds linearly to the incident light level over at least 3½ orders of magnitude with non-linear response above 60% of target saturation. With a wavelength window of 230 nm, resolution is about 4 nm with wavelength linearity better than 0.3%. Scan times as fast as 2 ms per frame were used.

28. Codding E.G. and Horlick G., "Application of AND and Exclusive - OR (XOR) Logic Operations to the Identification of Elemental Emission Spectra Using a Photodiode Array Direct Reading Spectrometer", Appl. Spectrosc. 27, 366 (1973).

Direct current arc emission spectra have been measured for 35 elements over a 140 Å range in the 3240 to 3380 Å region employing a monochromator self-scanned linear silicon photodiode array detector system. Each spectrum was reduced to a binary representative by compressing the spectral intensity information such that a logic 1 and a logic 0 represented the presence and absence of spectral features. It is shown that with the application of the logic operations AND and exclusive-or (XOR) it is possible to identify uniquely each of the 35 elemental emission spectra. The feasibility of extending the procedure to multicomponent spectra is illustrated and discussed.

29. Jackson K.W., Aldous K.M., and Mitchell D.G., "Simultaneous Determination of Trace Wear Metals in Used Lubricating Oils by Atomic Absorption Spectrometry Using a Silicon-Target Vidicon Detector", Appl. Spectrosc. 28, 569 (1974).

A multichannel atomic absorption spectrometer with a silicon-target vidicon detector was used for the simultaneous determination of trace metals in aqueous solution and in used lubricating oils. In most cases sensitivities were similar to those obtained by conventional single channel atomic absorption. Iron, magnesium, copper, and silver were simultaneously determined in lubricating oils and, although precision was somewhat poorer than that normally attained by A.A., it was adequate for this application. Good correlation was obtained between the vidicon method and a single channel method using a commercial atomic absorption spectrometer.

30. Horlick G. Codding E.G. and Leung S.T., "Automated Direct Current Arc Time Studies Using a Computer-Coupled Photodiode Array Spectrometer", Appl. Spectrosc. 29, 48 (1975).

A system based on a computer-coupled photodiode spectrometer has been developed which is capable of automatically acquiring and analyzing intensity-time data from a DC arc source. The intensity time curves for any desired lines can be plotted on a computer terminal within about two minutes after termination of the arc burn. The application of the system to some simple DC arc time studies is discussed and illustrated.

31. Horlick G., and Codding E.G., "Simultaneous Multielement and Multiline Atomic Absorption Analysis Using a Computer-Coupled Photodiode Array Spectrometer, Appl. Spectrosc. 29, 167 (1975).

By the use of a multielement lamp source and a computer-coupled photodiode array spectrometer, complete "atomic absorption spectra" are measured over a range of 130Å. Both quantitive and qualitative absorption information can be simultaneously acquired for lines of several elements and several lines of one element. Repetitive measurements of the spectral region being observed can easily be time-averaged under complete electronic control.

32. Winefordner J.D., Fitzgerald J.J., and Omenetto N., "Review of Multielement Atomic Spectroscopic Methods", Appl. Spectrosc. 29, 369 (1975).

A comparison of atomic spectroscopic methods and optical detection devices is given with respect to signal-to-noise ratio, experimental limits of detection, and other practical analytical figures.

33. Horlick G., "Characteristics of Photodiode Arrays for Spectro-Chemical Measurements", Appl. Spectrosc. 30, 113 (1976).

The operational characteristics and the measurement capability of a computer-coupled photodiode array spectrometer based on a 1024 element array are presented. This serves as a basic review of Horlick's previous work and provides a brief outline of the theory and applications of various electronic image sensors.

34. Jackson K.W., Aldous K.M., and Mitchell D.G., "Vidicon Television Camera Tubes for Atomic Absorption", Spectroscopy Letters, 6, 315 (1973).

The suitability of a vidicon TV tube as a detector for atomic absorption spectrometry was investigated. The spectral response was seen to be adequate throughout the range 217.0 - 313.8 nm. The instrument was then used as a detector in operation. The spectral response of the vidicon was evaluated by comparing it with that of an R106 photomultiplier. Signals were observed for the same time in each case, calibration graphs were obtained, and comparative sensitivities, precision, and detection limits were recorded. The sensitivities are comparable, but the signal-to-noise ratio with the vidicon was poorer and it is explained that this may be due to a fundamental difference between the detector used and a photomultiplier in that no amplification occurs within the vidicon tube.

35. Codding E.G. and Horlick G., Spectroscopy Letters, 7, (1974).

A further study of the computer coupled photodiode spectrometer. In this note the authors report on an improved system over that used in Reference 28 - for simultaneous multi-element quantitative analysis with a dc arc source. The simultaneous measurement of a number of analytical curves for several elements in a synthetic brass sample was carried out. Analytical curves were established using computer controlled background subtraction, but no internal standards were required. Spectra representing sequential time integrated segments of a total arc burn could readily be acquired and stored in the computer. They conclude that they are working on a process for completely automating the time study of a sample with this system.

36. Boumans P.W.J.M., and Grouwer G., "Studies of Photodiodes and Phototransistors as Detection Devices for Multichannel Emission Spectrometry", Spectrochimica Acta, 27B, 247 (1972).

A one-dimensional array of phototransistors was tested as a device for measuring intensities at closely-spaced wavelengths in the focal plane of the spectrometer. The detector consists of an array of some 20 equally-spaced silicon phototransistors.

37. Boumans P.W.J.M., Rumpjorst R.F., Willemsen L. and De Boer F.J., "Solid State Photodiode System Matched to High-Gain Low-Noise D.C. and Lock-In Amplifiers for Use in Multichannel Emission Spectrochemical Analysis", Spectrochimica Acta, 28B, 227 (1973).

Various configurations of planar silicon photodiode arrays were tested as detection devices for multichannel emission spectrometry. A perfectly linear response over at least three orders of magnitude above the noise level and a spectral resolution equivalent to that attained with photomultiplier and exit slit were established. Comparison of the signal-to-noise ratio (S/N) of the photodiodes with that of various types of photomultipliers showed that photomultipliers were superior by a factor of 100-500 in the S/N at low light levels in the wavelength region between 2500 and 5500 Å. In order to match the detectors to the amplifiers, they worked with photodiodes and not with phototransistors as in the previous study.

38. Beaver E.A., and McIlwain Carl E., "A Digital Multichannel Photometer", The Review of Scientific Instruments, 42, 1321 (1971).

An early report on the application of semiconductor detectors. A semi conductor diode image tube system has been built which has the characteristics of a good photomultiplier tube but which can simultaneously measure light intensity at 38 different positions. Tube dark current is 0.02 count/sec./position. "A tube with up to 1000 elements appears feasible. The digital multi-channel photometer approach should yield results comparable with a photomultiplier tube array with pulse counting electronics at much less cost, weight, and size." One future use mentioned is in low light level astronomy.

39. Staff Report, "Frontiers in Radiation Detection", Research/Development, 23, 24 (1972).

The advantages of semiconductor materials other than silicon and germanium are presented. Substances such as cadmium telluride, gallium arsenide and mercuric iodide show promise as room temperature detectors in the future, while silicon and germanium units are being improved. However, the silicon and germanium detectors currently remain more accurate and more reliable because of slow developments in the production of other semiconductors.

40. Knapp D.O., Omenotto N., Hart L.P., Plankey F.W., and Winefordner J.D., "Simultaneous Multielement Atomic Emission Flame Spectrometry With an Image Vidicon Detector", Analytica Chimica Acta, 69, 455, (1974).

A silicon diode array vidicon camera tube with enhanced UV response is used for the detection of the atomic emission of several mixtures of elements with rather complex emission spectra. The unit has several useful characteristics including broad spectral range (200-1100 nm), high quantum efficiency (>20% in the regions of 250 and 1000 nm, and <50% in the range 350-800 nm), linear response over a large range of fluxes ($\simeq 10^3$), low geometric distortion, and the possibility of storing and subsequently subtracting the background from the data spectrum.